Novel, Combinatorial Method for Developing Cathode Catalysts for Fuel Cells

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Project ID: # FCP30

Overview

Timeline

- Start Date: October, 2004
- End Date: December, 2007
- 75% Completed

Barriers

- Low activity of non-Pt catalysts
  - 2004 Status: 8 A/cm^3
  - 2010 Target: >130 A/cm^3

Budget

- Phase II SBIR
- Total Project Funding
  - $750,000
- 2005 Funding: $246,000
- 2006 Budget: $420,000

Partners

- Illinois Institute of Technology

Need for New Fuel Cell Cathode Catalyst

- **Automotive Applications:**
  - Order of magnitude improvement over current Pt alloy based MEA's.
  - Cost – $10/kW MEA Cost
  - High Efficiency – 0.2 g/peak kW total anode/cathode loading.
  - Long Life – 10-15 years life

Project Objectives

- Develop a controlled method for accurate high-throughput evaluation of new catalyst materials.
- Scale up combinatorial approach: Sample preparation, screening system and data processing.
- Evaluate several families of catalysts for oxygen reduction activity.
- Scale up new, low-cost high-activity catalysts for evaluation in fuel cells.
- Develop instrument for efficient evaluation of multiple fuel cell components (catalysts, membranes, MEA’s, etc) for general use in process development and manufacturing quality control.

Why Combinatorial Approach for Catalyst Development?

- **Barriers to rational design.**
  - Complex surface chemistry.
  - Lack of a complete understanding of the reaction processes involved.
- **Many possible catalyst permutations (not confined by equilibrium phases).**
- **Screening in parallel allows for better evaluation of relative performance.**
- **Can potentially greatly reduce the cost of optimization and accelerate the discovery of new catalysts.**

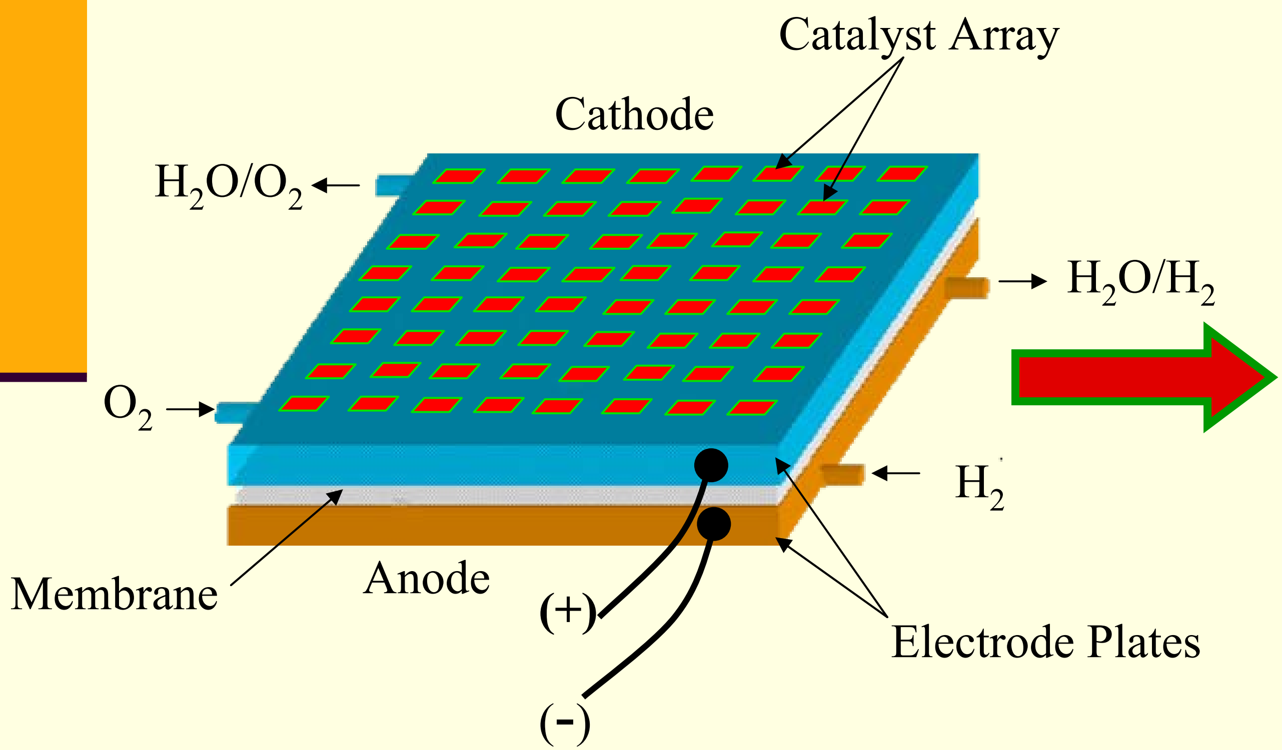
Phase II Project Catalyst Development Strategy

- Identify best chemistry first then optimize for utilization.
- Control all critical parameters to determine inherent catalyst activity.
- Use systematic DOE techniques to design catalyst array compositions and testing condition variables.

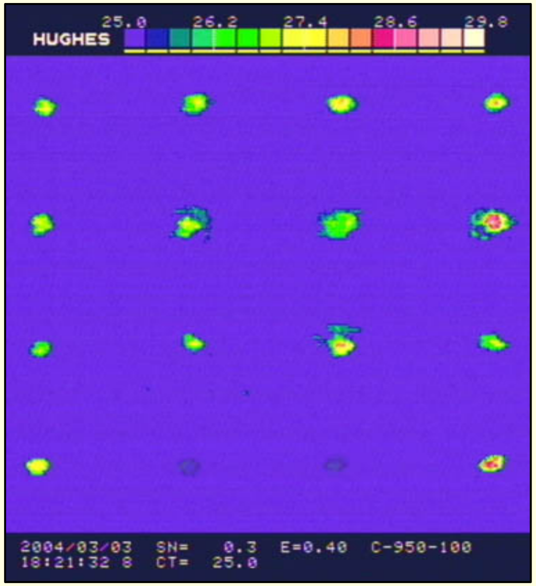
Technical Approach

Thermal Sensing

Thermal sensing allows for in-situ monitoring of individual catalysts samples in a closed fuel cell system.



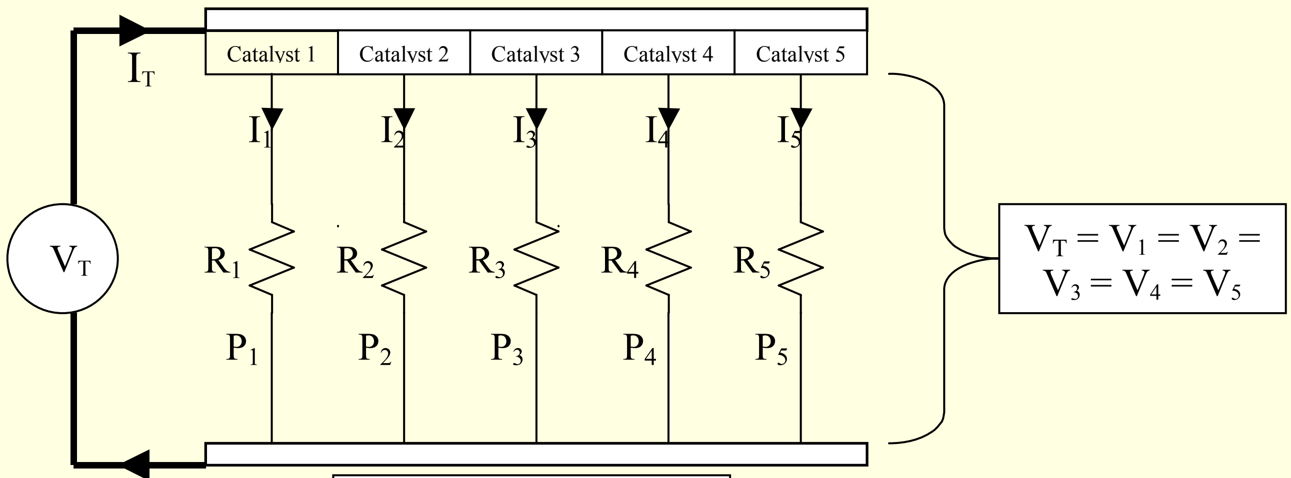
Thermal Image



Heat Generation and Catalyst Efficiency

- **Correlation between i^2R heat generated and current density.**
- **The best catalyst will generate the most heat.**
- **The current passing through each sample can be determined from dT.**

$$\text{(1)}\quad \Delta T_x \propto P_x = I_x^{\,2} R_x = I_x V_T$$

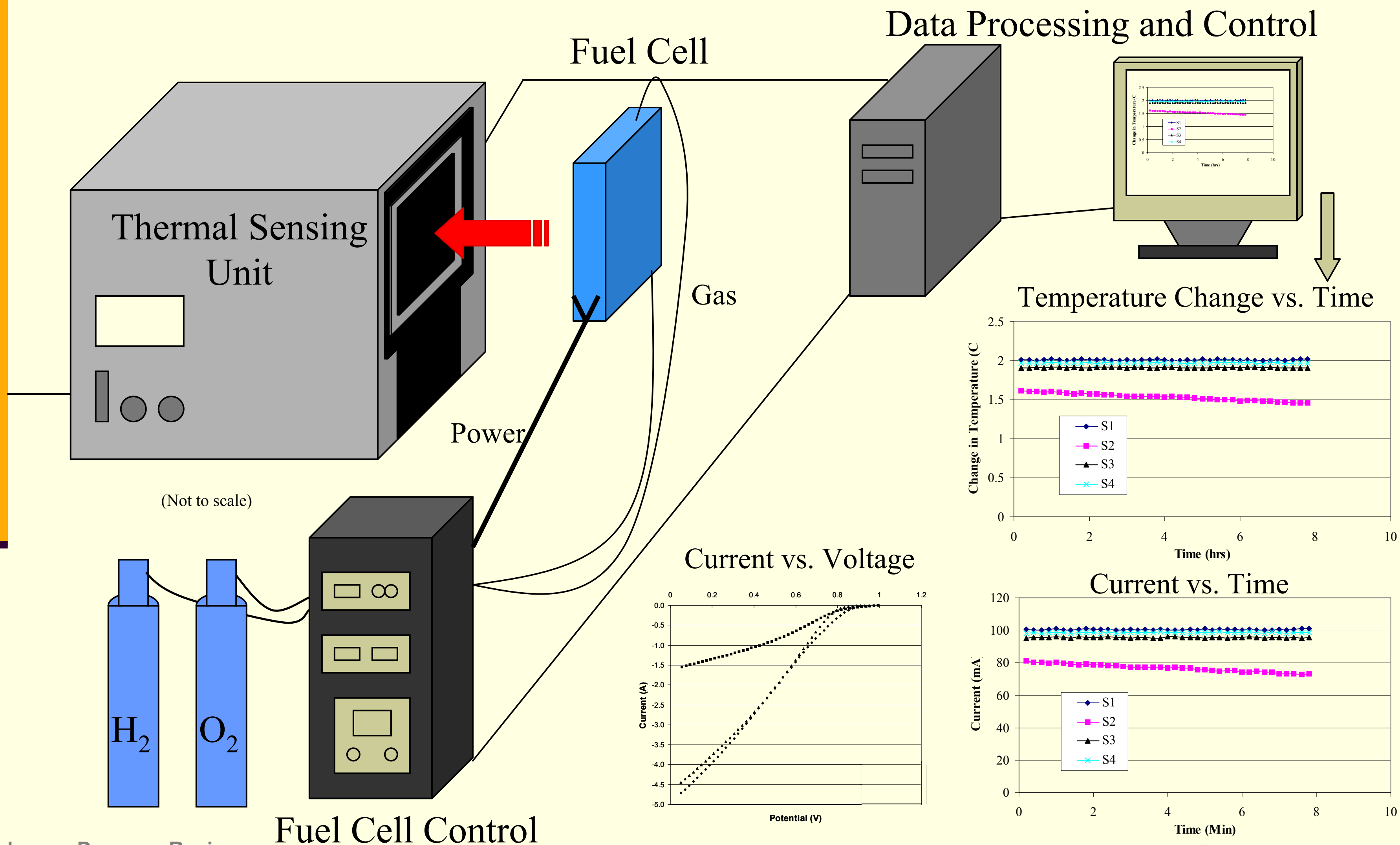


$$I_T = I_1 + I_2 + I_3 + I_4 + I_5$$

$$\text{(2)}\quad V_T = R_1 I_1 = R_2 I_2 = \ldots\ldots$$
$$\text{(3)}\quad I_1 = (R_2/R_1) I_2, \ldots.$$

Platinum/0.2V ~ 10^{-3} W/cm^2
Carbon/0.2V ~ 10^{-6} W/cm^2

Fuel Cell Catalyst Screening System



Technical Approach Advantages

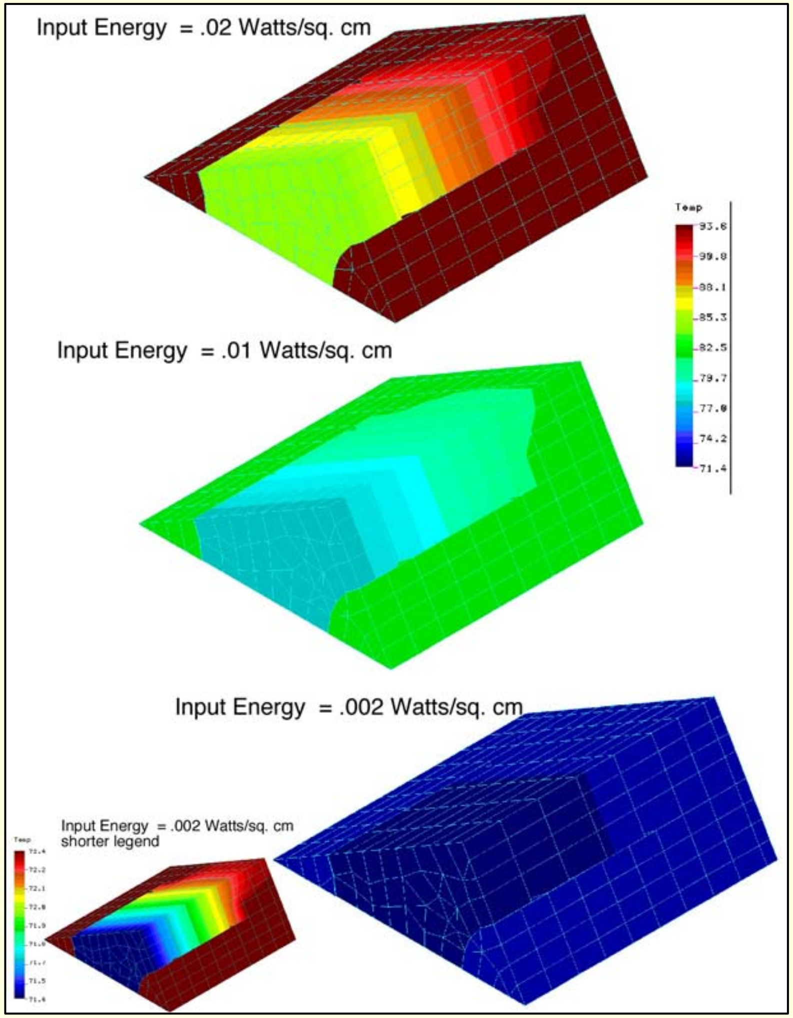
- In-situ screening under real operating conditions.
- Good control of critical parameters that affect performance.
- Great flexibility to screen any catalyst type for any fuel cell system.
- Simple, low-cost system scale-up.

Technical Accomplishments/ Progress/Results

- **Finalized Gen 1 screening system design and verified performance.**
  - Uniform stack pressure.
  - Uniform fuel distribution.
  - Uniform heat signal.
- **Prototype Gen 2 screening system developed.**
- **Developed high-throughput sample preparation system.**
- **Exploration of catalyst families.**
- **Detailed characterization of binary Pd-Co catalyst system.**

Thermal Modeling to Aid System Design

- **Developed design in miniature before scale up.**
  - 35 cm^2 array cell.
  - Accelerates development cycle.
  - Lowers cost of development.
    - Smaller MEA's
    - Fewer Samples.
    - Less Labor.



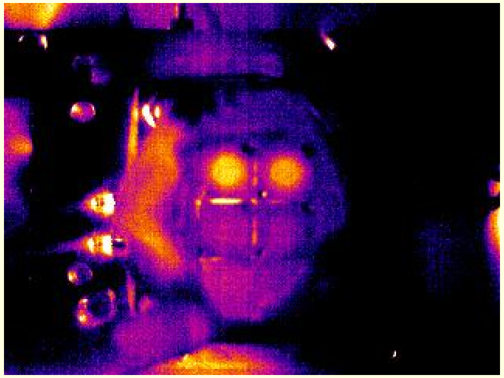
Qualifying Gen 1 System Design

- **Qualify on 4-sample array apparatus before scale up.**
- **Qualification Procedure.**
  - Demonstrate correlation between current and temperature.
  - Verify uniform fuel flow.
  - Verify uniform stack pressure.
  - Verify evaluation of constant catalyst surface area across array.
- **Scale-up to 25-sample array apparatus.**
- **Catalyst Screening.**

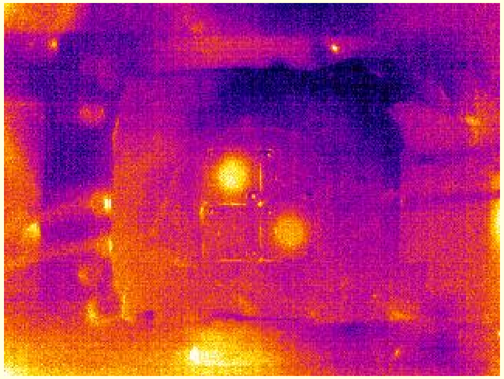
Gen 1 System: Thermal Signal Correlations

4-Sample Array

2x Pt (top) vs. 2x Carbon (bottom)

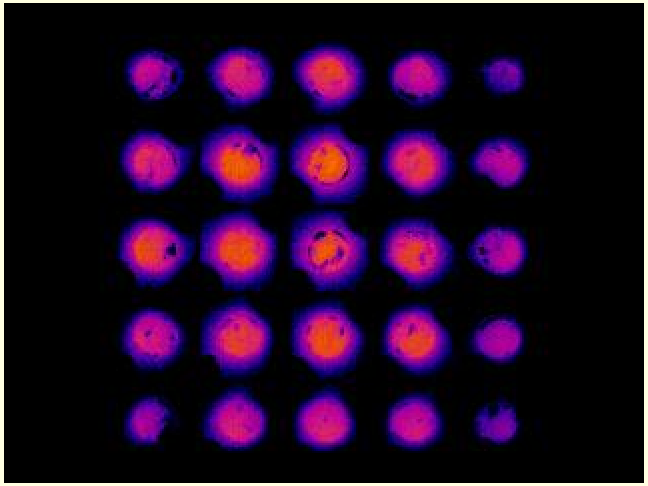


After switching right-side samples



25-Sample Array

- 55 °C Operation
- H_2/O_2
- Binary array
- $\Delta T \sim 2°C$
- Hot spots – highest activity

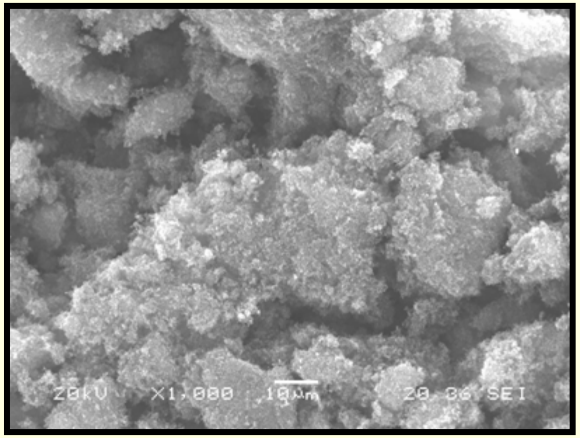


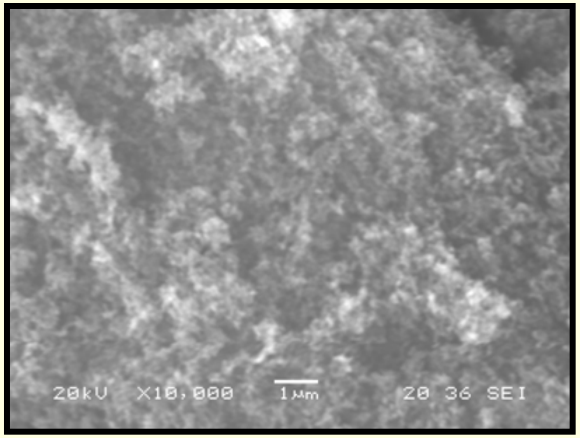
Stage 2 Catalyst Development

- Best identified catalyst families are further characterized by conventional methods.
- Electrodeposited catalyst samples – CV's, Rotating Disk.
- Carbon supported catalyst – MEA's, H_2 fuel cell.

Preparation and Characterization of Carbon Supported $CoPd_x$ Electrocatalysts

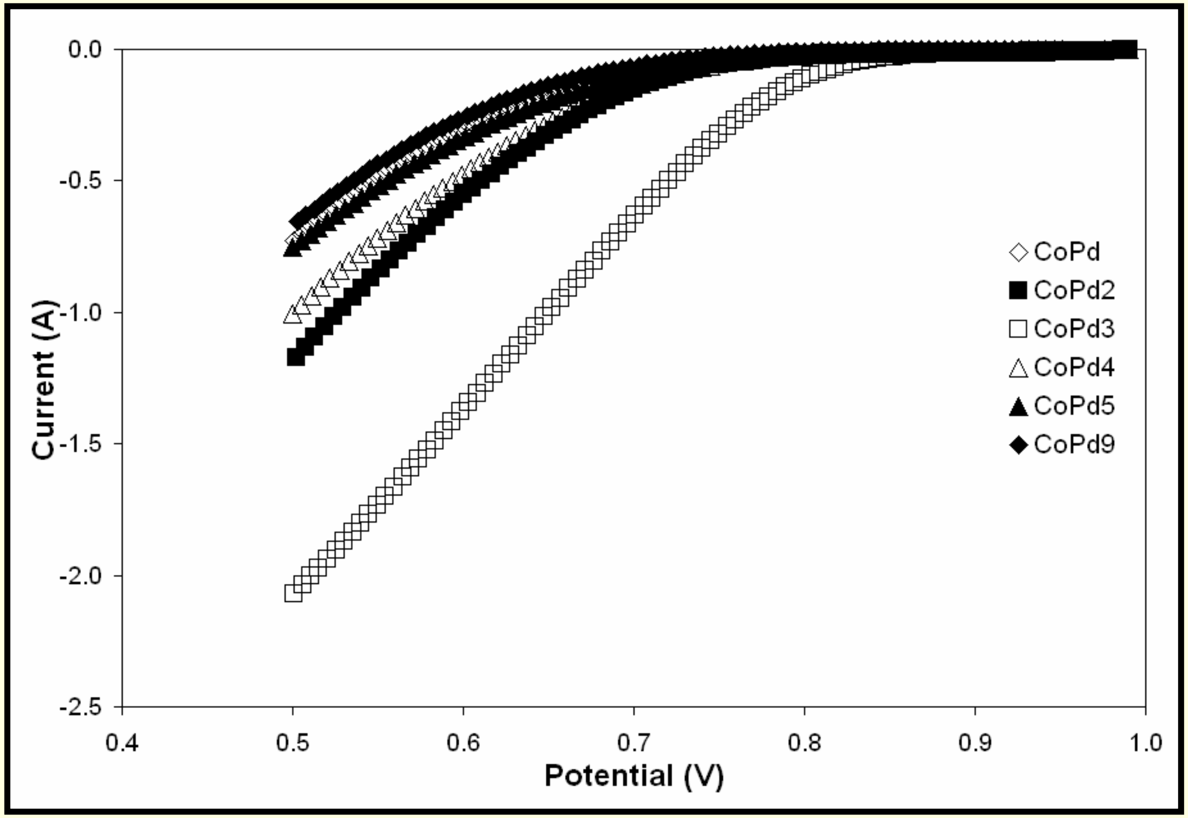
- **Preparation**
  - Deposit Salts using Sodium Bicarbonate as reducing agent. $Co[NO_3]_2*6H_2O$, $Pd[NO_3]_2$
  - Catalyst filtered, rinsed, vacuum dried and activated in a $2\%H_2$, $98\%Ar$ atmosphere for 24 hours.
  - Loading 10 wt % $CoPd_x$ on Vulcan XC72R
- **Characterization**
  - SEM/EDX, BET





Co-Pd Catalyst Family with High Activity

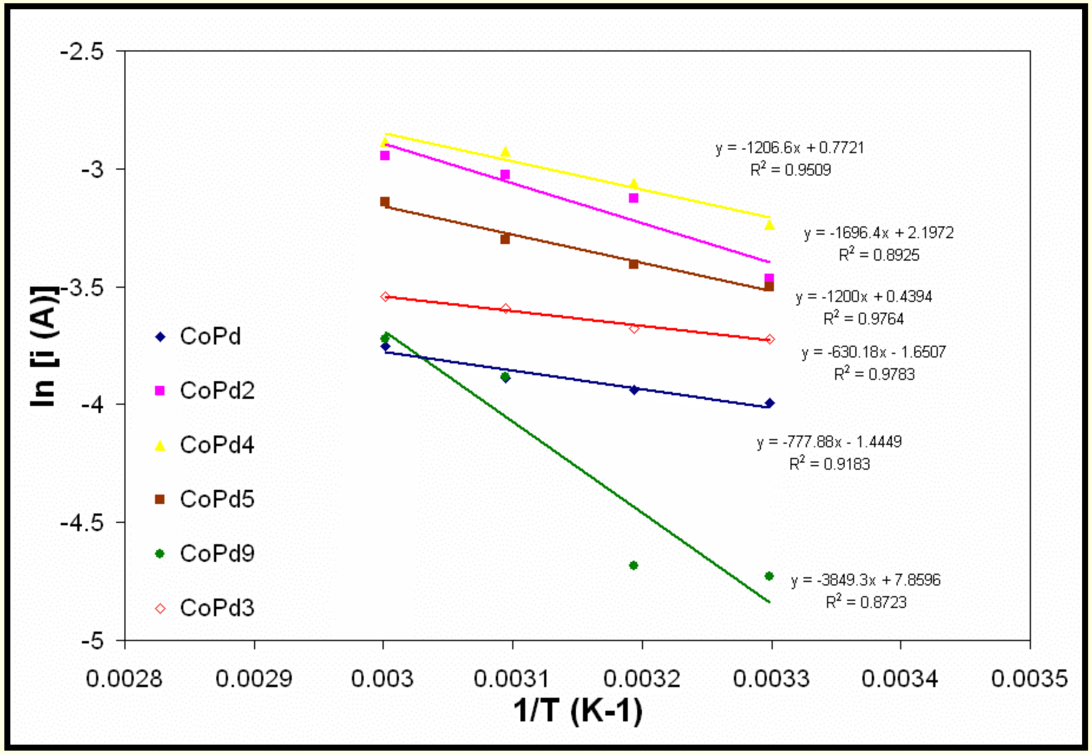
Polarization Curves for Co-Pd compositions



- Temperature: 60^{o}C
- Cathode gas: O_2
- Anode gas: H_2

$CoPd_x$ Kinetic Parameters

Arhenius Plots for the ORR in a 5 cm² PEMFC on $CoPd_x$ Electrocatalysts

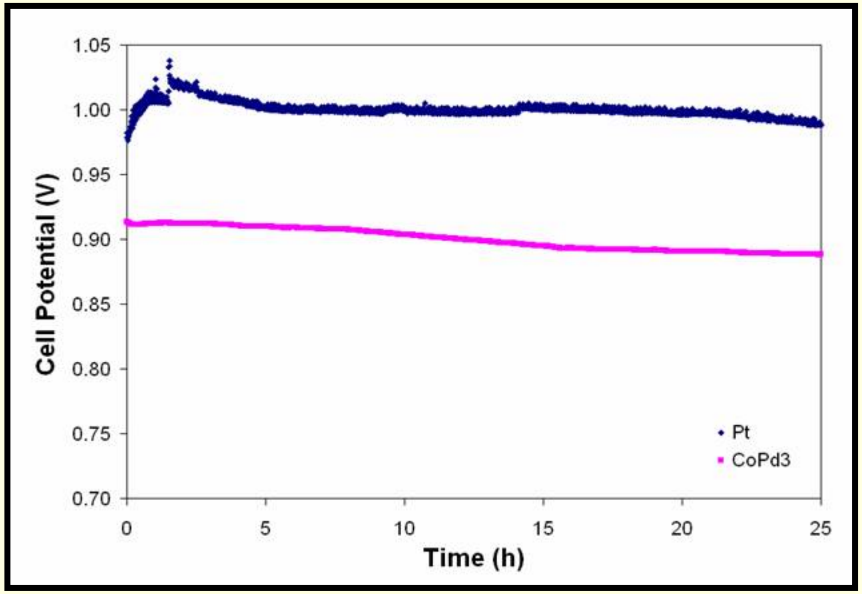


Calculated Kinetic Parameters for ORR on $CoPd_x$ Electrrocatalysts in a H_2/O_2 PEMFC

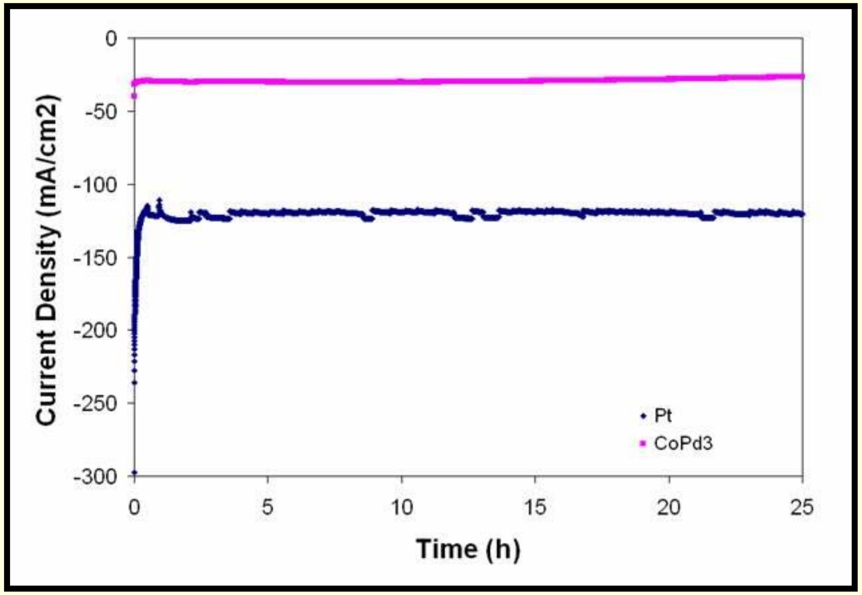
Composition	Onset Potential (V)	Activation Energy (kJ/mol)	Tafel Slope, b 60°C (mV/dec)	Exp[a/b]
CoPd	0.87	80.4	96.5	4.08E+02
$CoPd_2$	0.88	104.0	87.1	1.23E+03
$CoPd_3$	0.92	52.4	69.6	2.69E+04
$CoPd_4$	0.89	100.3	90.3	7.69E+02
$CoPd_5$	0.90	99.8	100.1	2.43E+02
$CoPd_9$	0.89	320.0	34.8	1.72E+08

Performance Stability of Pd_3Co in Hydrogen Fuel Cell

Open Circuit Voltage Pt and $CoPd_3$-cathode/ Pt-anode MEAs in a 5 cm^2 PEMFC at 60 ^oC.



Performance Stability of Pt and $CoPd_3$ cathode MEAs at 0.8 V, 60 ^oC.



• Some performance degradation of $PdCo_3$ catalyst observed.

Future Work

- Scale up Gen 1 screening system to 50-100 samples/cell.
- Scale up Gen 2 screening system.
- Continue large scale screening of non-noble metal catalysts.
- Verify results in standard fuel cells.
- Continue Pd-Co development.

Summary

- We have developed an easily scalable method of combinatorially screening materials for electrochemical systems based on their efficiency related thermal signature.
- We are using this system to evaluate catalysts for oxygen reduction activity.
- Materials with the greatest potential are further characterized and optimized by conventional methods.
- Our combinatorial technique and development strategy greatly increase our probability of success and decrease our discovery time.

Publications

- Mustain, W.E.; Kepler, K. D.; Prakash, J.; "Investigations of Carbon-Supported $CoPd_3$ Catalysts as Oxygen Cathodes in PEM Fuel Cells", Electrochemistry Communications, 8 (2006) 406-410.
- Mustain, W.E.; Kepler, K. D.; Prakash, J.; "$CoPd_x$ Alloys as Oxygen Reduction Electrocatalysts for Polymer Electrolyte Membrane and Direct Methanol Fuel Cells", submitted for publication.